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From the kinetic data a new sorption equilibrium isotherm is derived
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## Summary

The sorption of gaseous methanol on cellulose has been studied at 30, 35, and 45°C. The process follows a second order equation and has an activation energy of 5,700 cal. per mole. A mechanism for the sorption process is suggested involving adsorption of methanol on the surface followed by permeation of the solid by methanol molecules. The kinetic data require that the surface adsorption be of the multilayer type. From the kinetic data a new sorption equilibrium isotherm is derived which fits the experimental equilibrium data over the entire pressure range studied, from a relative pressure of 0.1 to a relative pressure of 0.9. From this equation and from data for the adsorption of tertiary butyl alcohol on cellulose it is shown that most of the methanol held by cellulose is dissolved in the cellulose.

## Introduction

For the sorption of methanol on coal, it was found that the weight of methanol taken up at time t at some constant pressure and at constant temperature was given by the equation

$$W = \frac{k_x W_e^2 t}{1 + k_x W_e t}$$

In this equation W is the weight of methanol held by one gram of coal at time t, $k_x$ is the experimental velocity constant, and $W_e$ is the maximum weight of alcohol held by one gram of coal at the given temperature and pressure. The experimental velocity constant, $k_x$, was found to be independent of the pressure over a considerable range of pressure and hence is a true velocity constant in the sense that it is a function of the temperature only.

Limited data in the literature appeared to show that the same equation was valid for the sorption of polar gases on elastic wall gels such as cellulose. As cellulose is considered one of the precursors of coal it was thought desirable to investigate the kinetics of methanol sorption on cellulose in detail.

## Experimental

Apparatus: The sorption of methanol on cellulose was measured gravimetrically, using a McBain-Bakr type adsorption balance. The spring was made of Ni-Span-C wire and had a sensitivity of 1.57 milligrams per millimeter extension. Spring lengths were measured by a cathetometer to 0.1 mm. The sample, in the form of fibers, was carried in a glass bucket weighing around 200 milligrams. Sample weights were about 300 milligrams. The apparatus consisted of the balance, a

2-liter flask to add sufficient volume to the system so that during sorption experiments the methanol pressure did not vary more than 1 mm. Hg., a Hg manometer, and a storage flask for the methanol. Mercury sealed stopcocks were used throughout. The pumping system was a two-stage Hg diffusion pump backed by a mechanical pump. The entire apparatus was housed in an air thermostat whose temperature coul be held to ±0.1°C.

Chemicals: Absolute methanol, Mallinckrodt A.R. was used as received. It was stored over Drierite. Tertiary butanol was redistilled. The sample of cellulose was prepared for us by the Hercules Powder Co. Cotton linters were washed with NaOH solution, bleached with $Cl_2$ and then washed with distilled water. No further treatment of the material was made except that before the start of kinetic experiments a cellulose sample, after evacuation to constant weight, was allowed to remain in contact with methanol vapor for several days. The sorption of methanol on cellulose is isothermally reversible; evacuation of the system always caused the cellulose to return to a weight practically identical with the starting weight.

Procedure: After evacuation of the system until the cellulose sample showed constant weight, methanol vapor was admitted to the system and readings of the spring length taken at various times. The spring lengths were converted into weights making no correction for buoyancy which can be shown to be negligible or for adsorption of methanol on the glass bucket and spring. Experiments using an empty bucket showed that methanol adsorption on the glass bucket and the metal spring could be neglected up to relative pressures as high as 0.9. The fundamental data, then, are weights at known time intervals including the equilibrium weights characteristic of each pressure.

## Calculation of Velocity Constants

From the experimental data, a value of the fraction of the reaction, f, could be calculated for each value of the time. f is defined as $\dfrac{W_t - W_o}{W_e - W_o}$ where $W_o$ is the sample weight at time, t = 0, $W_t$ is the weight at t = t, and $W_e$ is the equilibrium weight at time t = ∞. The value of $\dfrac{f}{1 - f}$ was plotted against the time giving straight lines through the origin. The slope of this straight line is $k_x W_e$ and since $W_e$ is measured for each pressure and temperature $k_x$ can be calculated. In general, points fell on a straight line and the line passed through the origin. In all experiments readings were taken until at least 80% of the equilibrium sorption was attained. At low pressures, c = 0.1, experimental points corresponding to the initial stages of the reaction were above the straight line. This behavior will be discussed later.

## Experimental Data

The experimental values of $k_x$ and $W_e$ are tabulated in Table I.

Table I
Experimental Values, $k_x$ and $W_e$

| T (°C.) | c | $k_x \left(\dfrac{\text{gr. cellulose}}{\text{moles } CH_3OH\text{-hrs.}}\right)$ | $W_e \left(\dfrac{\text{moles } CH_3OH}{\text{gr. cellulose}}\right)$ |
|---|---|---|---|
| 30 | 0.894 | 5.8 x 10³ | 22.6 x 10⁻⁴ |
|  | 0.700 | 16.3 " | 18.1 " |
|  | 0.500 | 19.2 " | 13.6 " |
|  | 0.306 | 7.9 " | 10.0 " |
|  | 0.125 | 2.5 " | 5.3 " |
| 35 | 0.848 | 16.4 " | 21.1 " |
|  | 0.669 | 21.4 " | 17.3 " |
|  | 0.486 | 29.0 " | 12.9 " |
|  | 0.268 | 13.0 " | 8.8 " |
|  | 0.119 | 1.9 " | 5.1 " |
| 45 | 0.863 | 9.3 " | 21.2 " |
|  | 0.697 | 26.7 " | 16.9 " |
|  | 0.491 | 31.0 " | 13.1 " |
|  | 0.294 | 13.1 " | 8.8 " |
|  | 0.088 | 1.9 " | 4.5 " |

It will be noted that the value of the experimental velocity constant passes through a maximum as the relative pressure, c, decreases.

Since a true velocity constant, k, must be a function of temperature only, the experimental velocity constant, $k_x$, must be equal to k multiplied by some function of the relative pressure, c. Separation of k from $k_x$ requires that a mechanism of the process be formulated. Even such an operation does not insure that k is actually known because both velocity constants and equilibrium constants have a similar dependence on temperature. In other words, independent equilibrium data are needed to make sure that the term k is really not k multiplied by an equilibrium constant.

It will be necessary to anticipate the discussion of the mechanism for the sorption process to be given later. It is postulated in brief that the mechanism of the sorption process is a two-step process. The first step, known experimentally and theoretically to be rapid, is the adsorption of methanol molecules on the surface of the cellulose. The second step, which determines the reaction rate as the slower step, is the migration of methanol from the surface into the interior. From this type of a mechanism it is necessary that in the simplest case

$$k_x = k\,\Theta$$

where $k_x$ is the experimental velocity constant, k is the true velocity constant and $\Theta$ is the fraction of the surface sites covered.

Now the surface adsorption of methanol on cellulose can be of two types: monomolecular with one methanol molecule on one site or polymolecular with more than one methanol molecule on one site. For monomolecular adsorption, the Langmuir adsorption isotherm holds and it can be shown that $\Theta$ increases as c increases for all values of c. Since $k_x$ goes through a maximum, $\Theta$ likewise must go through a maximum as c increases. Consequently the surface adsorption of methanol on cellulose cannot be monomolecular. For polymolecular adsorption, the only alternative, the surface adsorption at a given temperature will be shown to be given by the equation

$$\Theta_n = \frac{(K_2)^{n-1} K_1 (c\,p^0)^n (1 - K_2 p^0 c)}{1 + K_1 p^0 c - K_2 p^0 c}$$

In this equation $\Theta_n$ is the fraction of surface sites covered by n molecules and $K_1$, $K_2$ are equilibrium constants whose significance will be discussed later. c is the relative pressure and $p^o$, the vapor pressure of methanol at the temperature in question. The product, $cp^o$, is the pressure of methanol vapor actually present. Insertion of values of one, two, or three for n gives $\Theta_1$, $\Theta_2$, $\Theta_3$, the fraction of surface sites covered by one, two, or three molecules. It will be noted that the expression for $\Theta_n$ contains two parameters, $K_1$ and $K_2$. From three kinetic experiments at different values of c but at the same temperature, k, $K_1$, and $K_2$ can be evaluated in turn for $\Theta_1$, $\Theta_2$, $\Theta_3$.

In figure I is shown a plot of $\Theta_n$ as a function of c for n = 1, 2, 3, 4. It was found that the experimental values of $k_x$ used in the equation, $k_x = k \cdot \Theta_2$ gave the best fit of the experimental data. Figure II is a plot of $k\Theta_2$ against c. The points are the experimental points. The solid line is the calculated line using $8.1 \times 10^4$ as the value of k ($k_{true}$) at 30°C.

The values of $K_2 p^o$ evaluated at three temperatures are 1.07, 1.03, and 1.05. These values of $K_2 p^o$ are sufficiently close to one that these kinetic data are experimental evidence for the correctness of the assumption, $K_2 p^o = 1$, made in the derivation of the BET equation.

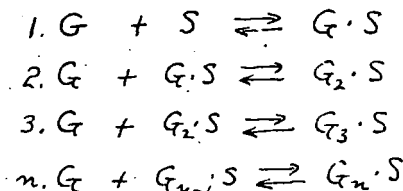With this assumption, the equation for $\Theta_2$ simplifies into

$$\Theta_2 = \frac{K_1 c^2 p^o (1 - c)}{1 + (K_1 p^o - 1) c}$$

From this equation and from the equation, $k = k_x \Theta_2$, the values of $K_1$ and k can be obtained. However the values of $K_1$ can also be obtained from the equilibrium isotherm and as the equilibrium measurements have the higher precision, it seems desirable to use these values in calculating k. The values of $K_1 p^o$, as evaluated from the equilibrium isotherm at 30, 35, and 45°C. are 3.0, 3.6 and 4.2 respectively. The corresponding average values of k in units of $\frac{\text{grams cellulose}}{\text{moles CH}_3\text{OH} - \text{hours}}$ for the three temperatures are: at 30°C., $8.1 \times 10^4$; at 35°C., $10 \times 10^4$; and at 45°C., $12.7 \times 10^4$. These values substituted in the Arrhenius equation give 5,700 cal. per mole as the average energy of activation. This low value for the energy of activation is evidence that the sorption process is physical in nature.

### Equilibrium Sorption Isotherm

The full solution of the kinetic problem in closed equation form requires that $W_e$, the equilibrium sorption, be expressed as a function of the relative pressure, c, and the temperature, T. The kinetic data are informative and permit the derivation of an equation for the equilibrium sorption isotherm. The sorption of methanol by cellulose can be visualized as a two-step process: 1. Adsorption of methanol on the surface, and 2. Migration of methanol from the surface into the interior.

For the surface adsorption, the following equations hold:

$$1. \; G + S \rightleftharpoons G \cdot S$$
$$2. \; G + G \cdot S \rightleftharpoons G_2 \cdot S$$
$$3. \; G + G_2 \cdot S \rightleftharpoons G_3 \cdot S$$
$$n. \; G + G_{n-1} \cdot S \rightleftharpoons G_n \cdot S$$

In these equations G represents the gas molecule; S the surface sites; G·S, the surface sites holding one gas molecule; $G_2$·S, the surface sites holding two gas molecules, etc.

If $\theta_1$ represents the fraction of surface sites holding one molecule; $\theta_2$, the fraction of surface sites holding two molecules; $\theta_n$, the fraction of surface sites holding n molecules; then the equilibrium constants would be expressed as

$$K_1 p^o = \frac{\theta_1}{(1 - \theta_1 - \theta_2 \cdots \theta_n)c}$$

$$K_2 p^o = \frac{\theta_2}{\theta_1 c}$$

$$K_n p^o = \frac{\theta_n}{\theta_{n-1} c}$$

where $p^o$ is the vapor pressure of the liquid and c is the relative pressure.

Further manipulation of these equations requires some simplifying assumptions connecting the equilibrium constants. If it is assumed that $K_1 > K_2$ and $K_2 = K_3 = K_n$, two assumptions similar to the ones made in derivation of the BET equation (1), then it can be shown that

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1. S. Brunauer, P. H. Emmett, and E. Teller, J. Am Chem. Soc., **60**, 309 (1938)

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$$\theta_1 = \frac{K_1 p^o c (1 - K_2 p^o c)}{1 + (K_1 - K_2) p^o c}$$

$$\theta_2 = K_2 p^o c \, \theta_1$$

$$\theta_n = (K_2 p^o c)^{n-1} \theta_1$$

These equations were applied to the kinetic data and it was shown that the kinetic data make two facts obvious: 1. The adsorption of methanol on cellulose involves more than one molecule for one surface site, and 2. $K_2 p^o = K_3 p^o = K_n p^o = 1.0$.

To determine the adsorption isotherm a term, $\Sigma$, will be defined as

$$\Sigma = \theta_1 + 2\theta_2 + 3\theta_3 \cdots + n\theta_n$$

$\Sigma$ is a concentration unit representing moles of adsorbed molecules for $6.02 \times 10^{23}$ occupied sites or one mole of sites. It has been shown (1) that $\Sigma$ is given by the equation,

$$\Sigma = \frac{\theta_1}{(1 - K_2 p^o c)^2}$$

and using the condition that $K_2 p^o = 1$ this equation reduces to

$$\Sigma = \frac{\theta_1}{(1-c)^2} = \frac{K_1 p^o c}{(1 + (K_1 p^o - 1)c)(1 - c)}$$

which is essentially the BET equation, for multiplying $\Sigma$ by a constant representing moles of sites for one gram of solid gives $W_e$, the equilibrium adsorption in moles per gram.

The second stage of the sorption process involves the migration of molecules adsorbed on the surface into the interior. This reaction can be represented by the equation,

$$CH_3OH \, (surface) + D \rightleftarrows D \cdot CH_3OH$$

In this equation D represents interior sites. Calling $\phi$ the fraction of D sites holding methanol molecules, the equilibrium constant, K, for the above reaction can be written as

$$K = \frac{\phi}{(1-\phi)\Sigma}$$

and solution of this equation for $\phi$ gives

$$\phi = \frac{K\Sigma}{1 + K\Sigma}$$

and the amount of sorption, $W_e$, is given by the equation

$$W_e = \frac{AK\Sigma}{1 + K\Sigma}$$

where A is moles of interior sites for one gram of solid. In setting up the last equation it has been assumed that the measured equilibrium sorption is the sorption on interior sites or, in other words, the surface adsorption contributes very little to the total sorption. An experimental and theoretical justification of this assumption will be given later.

It should be pointed out that the particular equation for $W_e$ is not the general form. The reaction involving sorption on internal sites might be,

$$n\, CH_3OH\, (surface) + m\, D \rightleftarrows D_m \cdot (CH_3OH)_n$$
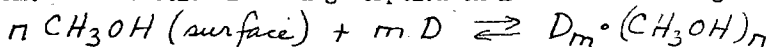
In all cases examined to date, $n = m = 1$. Furthermore it has been assumed by using $1 - \phi$ for the concentration of empty internal sites that the number of sites is independent of the amount of sorption. If sorption leads to the formation of new sites, by expansion of the gel, then the concentration of empty internal sites would be of the form, $(1 - \phi + f(\phi))$. To date, no definite experimental evidence has been found which requires the use of a site-expansion term.

The sorption isotherm derived here, which is

$$W_e = \frac{AK\Sigma}{1 + K\Sigma}$$

$$\Sigma = \frac{K_1 p^o c}{(1 + (K_1 p^o - 1)c)(1-c)}$$

is an equation involving three parameters, $A$, $K$, $K_1$. It has been found to fit the equilibrium data in the literature for the sorption of polar gases by elastic wall gels. The extension of this equation to other systems will be the subject of a subsequent paper. But it can be stated that in general it will fit many systems up to relative pressures of 0.9 or greater.

The equation fits the equilibrium data for methanol sorption on cellulose also to 0.9. Application of the equation to the methanol-cellulose system gives the constants listed in Table II.

### Table II
#### Constants for Methanol Sorption on Cellulose

| Temp. | $K_1$ | K | A |
|-------|-------|-----|-----------------------------|
| 30°C. | 14.51 atm.$^{-1}$ | 0.75 | 2.61 x 10$^{-3}$ moles D sites/ gram |
| 35 | 13.60 | 0.65 | 2.65 " " " " " |
| 45 | 9.91 | 0.58 | 2.64 " " " " " |

The values of K in Table II, are dimensionless because $\Sigma$, used in K, represents a dimensionless quantity, the average number of adsorbed molecules held by one occupied surface site. It will be noted that A is independent of the temperature
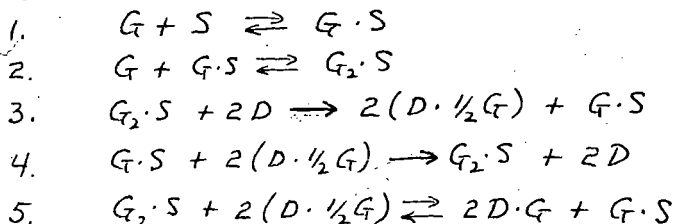
as would be expected. $K_1$ and $K$ vary in the normal manner with the temperature. Using the equation, $\Delta F^\circ = - RT \ln K$ , and evaluating $\Delta H$ from a plot of lnK against the reciprocal of the absolute temperature $\Delta F^\circ$, $\Delta H$ and $\Delta S$ for surface adsorption ($K_1$) and for interior sorption (K) can be evaluated. These quantities have been tabulated in Table III.

### Table III
### Thermodynamic Values

| Equilibrium | Temp. | $\Delta F^\circ$ | | $\Delta H$ | | | $\Delta S$ | |
|---|---|---|---|---|---|---|---|---|
| | 30°C. | -1610 cal./mole | | -5080 cal./mole | | | -11.5 cal./degree | |
| Surface | 35 " | -1600 " " | | " " " | | | -11.3 " " | |
| $K_1$ | 45 " | -1450 " " | | " " " | | | -11.4 " " | |
| | 30°C. | 530 cal./mole | | -1830 cal./mole | | | - 7.8 " " | |
| Interior | 35 " | 600 " " | | " " " | | | - 7.9 " " | |
| K | 45 " | 660 " " | | " " " | | | - 7.8 " " | |

Thermodynamic data derived from measurements over limited temperature ranges would be expected to have low precision so that conclusions drawn from such data cannot be too definite. The heat of condensation of methanol vapor in the temperature range from 30° to 45°C. is known to vary but assuming a constant value over this temperature range the heat of condensation is approximately -8,600 cal. per mole. The fact that the value of $\Delta H$ for the interior sorption (D sites) differs greatly from the heat of condensation indicates that the interior sorption cannot consist of a large number of methanol molecules clustered near one site. In general, clustering of methanol molecules so that interaction of methanol molecules with methanol molecules takes place should lead to higher values of the heat of reaction for the interior sorption than those observed.

### Reaction Mechanism

The following reaction mechanism is suggested for the kinetics of methanol sorption on cellulose:

1. $\quad G + S \rightleftarrows G \cdot S$

2. $\quad G + G \cdot S \rightleftarrows G_2 \cdot S$

3. $\quad G_2 \cdot S + 2D \longrightarrow 2(D \cdot \frac{1}{2}G) + G \cdot S$

4. $\quad G \cdot S + 2(D \cdot \frac{1}{2}G) \longrightarrow G_2 \cdot S + 2D$

5. $\quad G_2 \cdot S + 2(D \cdot \frac{1}{2}G) \rightleftarrows 2D \cdot G + G \cdot S$

Reactions 1 and 2 represent the adsorption of the gas on S (surface) sites. Obviously additional reactions leading to the formation of species like $G_3 \cdot S$, $G_4 \cdot S$ are also involved but are not necessary for explanation of the kinetic data. All reactions involving surface adsorption of the physical type are known to be rapid both on theoretical and experimental grounds. The double arrow is used to indicate that these reactions are in equilibrium.

Reaction 3 is the slow rate-determining reaction for the sorption process. A molecule from a site of the $G_2 \cdot S$ type migrates into the interior and is held on two D (internal) sites. Two internal sites are required to explain

the second order kinetics found experimentally. The nature of these sites will be discussed later. Reaction 4 is the reverse of reaction 3 and is necessary to account for the reversibility of the sorption process. Reaction 5 is a rapid equilibrium type reaction. It is postulated to have one G molecule held on one D site, which is indicated to be the case from the previously derived sorption isotherm.

Using W to be $W_t - W_o$ or the increase in weight at time, t, and $W_e$ to be $W_\infty - W_0$ or the increase in weight at infinite time, the differential equation for the process is,

$$-\frac{dW}{dt} = k_3 \theta_2 (W_e - W)^2 - k_4 \theta_1 (W)^2$$

Since f, the fraction of reaction, is $\frac{W}{W_e}$, this equation can be arranged to give

$$\frac{df}{dt} = k_3 \theta_2 W_e (1-f)^2 - k_4 \theta_1 W_e f^2$$

Let B designate the term, $\frac{k_4 \theta_1}{k_3 \theta_2}$ . Introduction of B gives

$$\frac{df}{dt} = k_3 \theta_2 W_e \left[ (1-f)^2 - Bf^2 \right]$$

which on integration and substitution of limits gives,

$$k_3 \theta_2 W_e t = \frac{1}{2\sqrt{B}} \ln \frac{1 - f(1 - \sqrt{B})}{1 - f(1 + \sqrt{B})}$$

Unfortunately, this equation is difficult to handle numerically because of the appearance of B in the ln term. However, the experimental data indicate, that at higher pressures corresponding to higher values of c, B becomes smaller since $\theta_1/\theta_2$ is 1/c. If B can approach a small number then the differential equation simplifies to

$$\frac{df}{dt} = k_3 \theta_2 W_e (1-f)^2$$

which on integration and substitution of limits give

$$k_3 \theta_2 W_e t = f/1-f$$

This latter equation was used for the calculation of rate constants setting $k_3 \theta_2$ = $k_x$ . The experimental work indicates that at low pressures (c = 0.1) the full equation should be used. For single experiments it has been shown that the experimental data fit the full equation using the trial and error method for the evaluation of B. However, the low pressure region from c = 0 to c = 0.1 is the region for which the experimental precision of the apparatus is low. This is the reason for limiting the experimental work to the region, $c > 0.1$ .

It will be noted that the data suggest only $G_2 \cdot S$ species on the surface furnish G molecules for the interior sites. The question naturally asked is why other types of surface species such as $G \cdot S$ and $G_3 \cdot S$ are not involved in the reaction. For the $G \cdot S$ configuration it appears that the G molecule is held more firmly on the S (surface) site than on the D (internal) site. The standard free energy differences at 30°C. for the reactions $G + S \rightleftarrows G \cdot S$ and $G + D \rightleftarrows G \cdot D$ are about -1600 and -450 cal. per mole, or a difference of 1150 cal. Two reasons can be advanced for the relatively little participation of $G_3 \cdot S$, $G_4 \cdot S$ species in the adsorption reaction. In the first place the fractions of surface, $\theta_1$ , $\theta_2$ , occupied by each type are related by the equation,

$$\theta_1 : \theta_2 : \theta_3 : \theta_4 = 1 : c : c^2 : c^3$$

and except at high values of c, the relative concentrations of $G_3 \cdot S$ and higher species are low. See Figure I. In the second place the adsorption sites on polymeric materials need not, as in the case of metals, be restricted to areas essentially equal to the area occupied by an atom. The area of the surface sites on cellulose could be much larger than the area of a single atom. Such sites could be visualized in the case of methanol adsorption on cellulose, as cooperative and hence adjacent functional groups such as hydroxyl. If this is true then the orientation of the surface units is of importance and the different types of sites correspond to adsorption on a heterogeneous surface. It is very probable that gaseous methanol molecules cannot penetrate the crystalline lattice of cellulose and where such a lattice is present on the surface, adsorption on such crystalline sites will not lead directly to sorption on the interior sites.

The reversibility of the sorption process is obviously dependent on the relative values of $\theta_1$, and $\theta_2$, which in turn depend on the pressure. If in the system at equilibrium the pressure of methanol is decreased, $\theta_2$ approaches zero faster than $\theta_1$, and the reverse reaction predominates.

### Desorption Experiments

The rates of desorption of methanol from cellulose have been measured in a number of experiments but with the experimental conditions used here the data are not significant and have not been reported. The desorption data follow the same rate equation as the sorption data. This can be shown by plotting $t/W$ against t. The slope of the straight line should be $1/W_e$. In desorption experiments all data fit on such a line. However the experimental slope is always lower than $1/W_e$, where $W_e$ has been determined from equilibrium measurements. Desorption experiments are made under high vacuum and as desorption is an endothermic process it is believed that in the present procedure the temperature of the sample is appreciably lower than the thermostat temperature. The present technique must be modified in some manner to get better heat transfer, probably by pelletizing the cellulose sample. Experimental work on this phase of the problem is continuing. It should be mentioned that in the sorption experiments $W_e$ as determined from the plot of $t/W$ against t always checked the value of $W_e$ obtained from equilibrium measurements to 1% or better. As the equilibrium measurement is free from thermal effects caused by the evolution of heat it was concluded that the sorption measurements were being made sufficiently close to thermostat temperatures so as to be significant. The low energy of activation for the sorption process indicates that the change in k with change in temperature is about 3% per degree in comparison to a change of greater than 6% per degree usually encountered in kinetic work.

### Number of Surface Sites

The kinetic data indicate that the number of surface sites on cellulose is small. The total weight of methanol held by cellulose at a given time must be equal to the weight of methanol on the surface plus the weight of methanol held in the interior. The experimental quantity is, of course, the total weight. Kinetically, it would appear that the only manner in which the total weight could follow the experimental kinetic equations would be that the weight of the methanol held in the interior is essentially equal to the total weight or that the weight of methanol adsorbed on the surface is small. If this is true, the number of surface sites on cellulose must be small. Experimental confirmation of this point is desirable.

The adsorption of tertiary butyl alcohol on cellulose has been measured at 45°C. Tertiary butyl alcohol was selected as a molecule having relatively large dimensions along the x, y, and z axis. The sorption of tertiary butyl alcohol by cellulose is a very slow process, and equilibrium values were not obtained because of the slowness of the system to come to equilibrium. The following procedure was adopted assuming that surface adsorption had reached its equilibrium value in one hour. For non-porous solids ten minutes suffices. The cellulose sample was exposed for one hour to a known pressure of tertiary butyl alcohol and the increase in weight recorded. The sample was then evacuated overnight and a new weight increase measured for a new pressure. Under these conditions, the cellulose sample returns to its initial weight on pumping so that the adsorption is reversible. Measurements of this type were made from relative pressures 0.1 to 0.8 and gave a Langmuir type isotherm. Tertiary butyl alcohol adsorptions ranged from $1.4 \times 10^{-5}$ to $7.9 \times 10^{-5}$ moles alcohol per gram cellulose. Except at low values of c, these values for tertiary butyl alcohol are much smaller than those obtained with methanol (see Table I). These data are considered experimental evidence that the number of surface sites on the cellulose is small and that most of the methanol held by the cellulose is dissolved in the cellulose.

## Acknowledgment

$\theta_n$ vs. c at 30°C

$\theta_2 k_{true}$ vs. c at 30°C

O — $k_{exp}$.